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Sources and sinks of acetone, methanol, and acetaldehyde in North Atlantic air

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Abstract

Measurements of acetone, methanol, acetaldehyde and a range of non-methane hydrocarbons have been made in North Atlantic marine air at the Mace Head observatory. Under maritime conditions the combination of OVOCs (acetone, methanol and acetaldehyde) contributed up to 85% of the total mass of measured non methane organics in air and up to 80% of the OH radical organic sink, when compared with the sum of all other organic compounds including non-methane hydrocarbons, DMS and OH-reactive halocarbons (trichloromethane and tetrachloroethylene). The observations showed anomalies in the variance and abundance of acetaldehyde and acetone over that expected for species with a remote terrestrial emission source and OH controlled chemical lifetime. A detailed model incorporating an explicit chemical degradation mechanism indicated in situ formation during air mass transport was on timescales longer than the atmospheric lifetime of precursor hydrocarbons or primary emission. The period over which this process was significant was similar to that of airmass motion on intercontinental scales, and formation via this route may reproduce that of a widespread diffuse source. The model indicates that continued short chain OVOC formation occurs many days from the point of emission, via longer lived intermediates of oxidation such as organic peroxides and long chain alcohols.

1. Introduction

Oxygen containing organic species such as aldehydes, ketones and alcohols have been identified as exerting a substantial effect on atmospheric oxidative capacity and are widely distributed throughout the depth of the troposphere. Their almost ubiquitous presence in the atmosphere has led to a number of studies aiming to recreate their behaviour using models, although discrepancies between some observed and calculated concentrations have led to the hypothesis that globally diffuse sources (such as sea-air exchange) may exist (Galbally et al., 2002; Singh, 2003). Apportioning sources of oxygenated compounds is complicated since they may be released as primary emissions from anthropogenic sources (e.g. acetone from solvent usage, acetaldehyde from combustion, methanol from biofuel), biogenic sources (possibly all three species), but also as by-products of atmospheric oxidation of hydrocarbon species. Their atmospheric lifetimes are relatively short (24 h–12 days), controlled by a combination of chemical, photolytic and physical removal processes and this has proved difficult to reconcile with their presence at both high altitudes and in remote locations. Many initial observations were made from aircraft, however datasets on longer time scales from ground observations are becoming available (Salisbury et al., 2003). There is still considerable uncertainty over sources and importantly whether the ocean plays a role in determining their abundance in maritime locations.

The remote observatory at Mace Head (53.3° N, 9.9° W), Ireland has been used on many occasions to study the long-range transport of atmospheric constituents of both natural and anthropogenic origin (Jennings et al., 1996; Lewis et al., 1997; Carslaw et al., 2000). In this study we have related abundance of acetone, methanol and acetaldehyde and a wide range of other organic species with airmass atmospheric trajectory over 5 days prior to arrival at Mace Head. We have paid particular attention to periods of 'clean marine air' where airmasses have had no terrestrial input for many days. Observations under these conditions have been combined with physical parameters such as wind speed, time an airmass spent close to the sea surface, and the origin of the airmass. The variability of oxygenated compounds with respect to tracers of known anthropogenic (e.g. benzene, carbon monoxide (CO)), terrestrial biogenic (isoprene) and oceanic (di-methylsulphide (DMS), organohalogens, alkenes) origin has also been examined and some conclusions on possible sources for this location made.

2. Methodology

The measurements reported here were made over a 40-day period using a combination of gas chromatography (GC) techniques covering a wide variety of organic species, allowing a relatively complete characterisation of organic constituents in air of maritime origin. The measurements were made as part of the North Atlantic Marine Boundary Layer Experiment (NAMBLEX) at the Mace Head Observatory between July and September 2002 (Heard et al., 2005[1]). C_2–C_7 hydrocarbons and small oxygenated molecules were determined using a dual channel Perkin Elmer GC-FID instrument coupled to a thermal desorption sampling system, see Hopkins et al. (2003) for full experimental detail. C_3+ oxygenates were measured using an Agilent 6890 GC with two independent columns connected via a valve modulator device (Hamilton et al., 2003). Halocarbons (trichloromethane, tetrachloromethane and carbon tetrachloride) were measured using a Perkin Elmer GC-quadrupole mass spectrometer operating in selected ion monitoring mode (Wevill and Carpenter, 2004). All samples were collected at shoreline from a height of 25 m through a low residence time 3/4 inch internal diameter manifold. Other members of the NAMBLEX group, although not reported explicitly in this paper made an extensive suite of measurements on other inorganic gases and aerosols some of which have been used to provide alternative confirmations of air mass origin and characteristics. Back trajectory calculations have been made by the British Atmospheric Data Centre based on ECMWF reanalysis of satellite wind field data.

Atmospheric production of methanol, acetone and acetaldehyde was investigated using a zero dimensional box model which incorporated mechanisms taken from the MCM v3 (Saunders et al., 2003). The aim of the study was to identify the key precursor species for these lightweight OVOCs and investigate the timescales of their formation, however, no attempt was made to recreate any of the concentrations observed at the Mace Head site. The model was initialised with background organic and inorganic content representative of fresh emissions leaving a continental landmass (with the exception that OVOC concentrations were initially set to zero) and left to evolve over a ten day period. Dilution was not considered in the model and hence are only an upper

[1]Heard, D. E. et al.: The North Atlantic Marine Boundary Layer Experiment (NAMBLEX), Mace Head, summer 2002, Campaign overview, Atmos. Chem. Phys. Discuss., in preparation, 2005.

limit of concentration within the airmass.

3. Results

3.1. Classification of Air masses

Although not always a good proxy for airmass origin, local wind direction gives a reasonable indication of frequency of cleaner westerly to more polluted easterly events. The polar plot of Fig. 1 highlights the significant number of samples from oceanic origins. Classification of air masses can be based on a range of gas phase and aerosol measurements. One such classification uses observations of OH and benzene and toluene, in conjunction with kinetic data to estimate the approximate age of an air mass arriving at Mace Head. If [OH] is assumed to be constant (calculated from a typical average OH concentration measured during westerly periods of the campaign) pseudo first order kinetics can be used to give:

$$\left(\frac{[\text{benzene}]}{[\text{toluene}]}\right)_{\text{MH}} = \left(\frac{[\text{benzene}]}{[\text{toluene}]}\right)_0 . \exp^{-(k_{\text{benzene}} - k_{\text{toluene}})[\text{OH}]t} \tag{1}$$

Where ([toluene]/[benzene])$_{\text{MH}}$ is the measured toluene:benzene ratio at Mace Head, ([toluene]/[benzene])$_0$ is the ratio at its emission source and t is the time in seconds that it takes to be transported from source to the Mace Head site. Although weaknesses exist in such a technique to quantitatively determine airmass age (McKeen et al., 1996) for determining clean sector observations the b/t ratio is highly sensitive to local fugitive emissions. Assuming a 4.4:1 ratio at source (London plume, summer 1988, Penkett et al., 1993), the ratio during the more polluted periods (JD 213-217) of 1:1 corresponds to a mean age of 72 h. In the oceanic westerly air masses at the beginning of the campaign (JD 205–209) the ratio was 1:3.7 leading to a calculated mean age of 139 h. Using a lower starting ratio reduces this airmass age for all classifications, but for this work we are simply interested in using this changing ratio as a marker for time since the airmass received a significant input of anthropogenic organic emissions. Calculations of this kind are notably sensitive to local inputs of fresh emissions and so can act as a check for the influence of local sources. Figure 3 shows the absolute concentrations of benzene and toluene and the calculated airmass age as a function of day of year. Observations have been further classified into airmass origin using both the local meteorological data and airmass back trajectories to assign particular geographic regions from which the airmass has been transported. Figure 3 shows the classes of trajectories used. The combination of these data allows for local effects such as sea breezes to be eliminated from grouped data classified as of clean marine origin.

3.2. Significance of oxygenated VOC

In air of polar, North American, and equatorial origins, organic composition was dominated by acetone, methanol and acetaldehyde, and this observation is similar to studies such as that of Boudries et al. (2002). The time series of concentrations is shown in Fig. 4, which is also annotated by airmass origin. The OVOC concentrations are similar to those previously reported in marine air and somewhat lower than observed at rural locations (summarised in Table 1). Reported mean values for acetone are significantly greater than a surface concentration of ~0.3 ppbV calculated by Singh et al. (1994) based on propane oxidation alone, implicating other precursors and sources. Large biogenic terrestrial sources have been proposed for methanol (∽113 Tg y^{-1}) and acetaldehyde from pasture and plants (Kirstine et al., 1998; Galbally and Kirstine, 2002; Kesselmeier, 2001) and biomass burning sources may produce up to 10, 4 and 6 Tg y^{-1} of acetaldehyde, methanol and acetone, respectively (Holzinger et al., 1999).

In marine air at Mace Head, the sum of these three compounds contributed up to 85% of the mass of measured organic carbon (excluding methane) and up to 80% of the organic hydroxyl radical sink. OH sinks used in the calculation including organic compounds, methane, hydrogen and CO, under these conditions is shown in Fig. 5. (NO_x under maritime conditions is exceptionally low at Mace head and is not considered significant.) Figure 6 shows organic primary OH sink percentage as a function of time, where individual compounds have been normalised to propene reactivity and grouped by compound type using:

$$\text{propene-equivalent}(A) = \frac{C_A k_{OH}(A)}{k_{OH}(C_3H_6)} \quad (2)$$

where C_A is the concentration of VOC species (in pptV), k_{OH} is the rate constant for the reaction between species A and OH and $k_{OH}(C_3H_6)$ is the rate constant between propene and OH. In reactivity terms, only during periods of significant local isoprene input does the primary hydrocarbon reactivity dominate over that of acetone, methanol and acetaldehyde, and this can be clearly seen as diurnally varying phenomena in line with expected isoprene behaviour.

3.3. Variability-lifetime relationship

Based primarily on species with longer lifetimes Junge (1974) proposed that the following inverse relationship existed between the concentration of a particular species and its variability:

$$RSD_i = \frac{0.14}{\tau} \quad (3)$$

where RSD is the relative standard deviation (standard deviation divided by mean) and τ is the residence time in years using only its reaction with OH. In later years an exponential relationship was found to be more appropriate and can be improved upon if the standard deviation of the natural log (ln) of the concentration $S_{\ln X}$ is used instead of the relative standard deviation RSD. At long lifetimes and small variability they are roughly equivalent however $S_{\ln X}$ is more appropriate when variability is higher (Jobson et al., 1994, 1998).

$$S_{\ln X i} = A\tau_i^{-b} \quad (4)$$

$$\log_{10} S_{\ln X\,i} = \log_{10} A - b \log_{10} \tau_i \quad (5)$$

A log plot of $S_{\ln X}$ versus t gives two constants A and b, which vary with source and can be used in comparisons between datasets.

A constant value of 1×10^6 molecules cm^{-3} for OH concentration was used as this was the average daily concentration in NAMBLEX, this leads to some uncertainty in the coefficient A, but not in the dependence of $S_{\ln X_i}$ on t. The use of lifetimes rather than rate constants allows easy comparison to both Junge's relationship and other reported measurements. Rate constants from Atkinson et al. (1986, 1989) were used to calculate the hydrocarbon lifetimes. Figure 7 shows the dependence of $S_{\ln X}$ on photochemical lifetime for data collected in southwesterly conditions. Whilst some compounds (trichloromethane, C_2–C_4 alkanes, iso-pentane, acetylene and benzene), lie on the common trend line where b=−0.45, there are many outliers (not all shown for clarity), which do not follow this trend. For the most reactive hydrocarbon species such as ethene and propene variance is less than expected, driven by constant low background abundance, even in clean marine air, a result of slow effusion of these gases from the ocean surface to the atmosphere. Longer-lived species in general agree better with this relationship, although secondary species such as acetone, methanol and acetaldehyde are exceptions. For acetone the variance is greater than expected when compared against its lifetime with respect to OH. This may in part be explained by other highly significant loss routes considerably reducing atmospheric lifetime from that implied by OH only chemistry. This would include photolysis but also potentially deposition to the sea surface. Diffuse in situ production upwind adds a further complication, producing a likely decrease in the observed variance - crudely therefore one might expect acetone to lie on the left hand rather than right hand side of the linear fit.

For acetaldehyde the variance is less than expected given its relatively short atmospheric lifetime calculated only with OH chemistry. Possible explanations may therefore be similar to ethene and propene in that there is a diffuse emission of this species from the sea surface in westerly conditions. The same effect may be reproduced however by atmospheric production occurring relatively close to observation location.

For methanol once again the variance is less than expected given its atmospheric lifetime calculated only with OH chemistry. Photolysis in this case is not significant, and the ocean as a source may be ruled out given those observations reported in Carpenter et al. (2004). Indeed the lifetime with respect to oceanic destruction is broadly similar to that due to atmospheric [OH]. In this case it seems likely that the low variance may be attributed to diffuse production upwind of the measurement location.

Clearly only qualitative conclusions may be drawn from lifetime analyses for these species, but it is helpful if only to highlight that the processing and behaviour of these species is very different to that of a primary terrestrial emission. There are clearly uncertainties relating to photolysis history of the airmass, and most importantly the effect that the ocean may have on emission or destruction of these species.

3.4. Ocean-atmosphere exchange

A previous paper (Carpenter et al., 2004) using this dataset has demonstrated that under certain westerly atmospheric conditions, deposition of methanol to the sea surface was occurring. A three day period of Atlantic cyclonic activity with airmasses of similar geographical origin, and where the averaged surface wind speed changed substantially as the low pressure system evolved, allowed a comparison of trace gas concentrations as a function of changing averaged surface wind speed within the boundary layer. This was highlighted by a strong anticorrelation of methanol with dimethyl sulphide, with both species showing wind speed dependence indicative of air sea exchange. Neither acetaldehyde nor acetone showed similar behaviour to methanol during this period, and a tentative conclusion may be drawn that under these particular North Atlantic conditions the ocean was not acting as a sink. DMS concentrations varied greatly during the experiment and had a strong wind speed and boundary layer residence time dependence, and for this experiment could be taken as an excellent proxy for active air-sea chemical exchange. From the dataset of unperturbed marine airmasses, no statistically significant relationship could be seen between ocean exchange tracers such as DMS and acetaldehyde/acetone and it would seem that the ocean (in this region and at this time) was effectively neutral in influencing atmospheric concentrations of these two OVOCs

3.5. Modelling study

If direct terrestrial emission of oxygenated VOC (or rapid production following emission) were the sole source prior to long range transport, the concentrations of the most reactive oxygenated species such as acetaldehyde should be low, and with significant variance dependant on time from source to receptor. This was not recreated in our observations, and in the absence of an observable sea source (and with an active sink in the case of methanol), we have investigated the mechanisms for in situ atmospheric production of these species on longer timescales as an explanation for apparent persistence in the marine troposphere.

Along an air parcel trajectory the localised production rate is controlled by formation from the degradation of organic compounds, balanced by OVOC+OH destruction and direct photolysis. This has been studied from a chemical perspective using the Master Chemical Mechanism v3 (Saunders et al., 2003) initialised with background organic and inorganic content representative of fresh emissions leaving a continental landmass (Table 2). This zero dimensional box is allowed to chemically evolve over a period of 10 days, typical of very long-range intercontinental zonal transport, and the results can be seen in Figs. 8a, 9a and 10a for acetone, methanol and acetaldehyde, respectively. Acetone concentrations (Fig. 8a and b) were predicted to increase during the day and remain constant at night, where overall net increases in atmospheric concentration were still occurring at the end of the 10-day period. The rate of production had slowed markedly by the 10th day with the rate of formation approaching the rate of atmospheric removal by OH and photolysis. Methanol (Fig. 9a and b) behaved in a similar manner to acetone, with a steady build-up in concentration over time, but with net production occurring after 10 days. The sustained production of methanol is clearly due to its dominant precursor, methane, which is both long lived and globally distributed, but it is worth noting that the non-methane organic contribution to methanol production is still significant several days downwind. The increase in production rate of methanol to its maximum at around day 5 is driven primarily by increases in calculated [OH].

The profile for acetaldehyde (Fig. 10a and b) is significantly different to both methanol and acetone with an initial rapid increase in concentration and then net destruction over days 2–10. The key difference for acetaldehyde is its shorter atmospheric lifetime, where removal rate exceeds production with the exception of around midday. Although the calculated concentrations of acetaldehyde decrease downwind, the daytime production from intermediates helps mitigate some of these losses, extending the influence of this species for many days longer than would otherwise be the case.

Whilst not providing a rigorous estimation of absolute concentrations at any point in time, since dilution and mixing are ignored (particularly important to methanol and acetone which almost certainly have non-zero background concentrations), this model allows for the important precursor species in the production process, the rate determining steps, and reservoirs of stable intermediates to be identified. It also provides a guide to the timescales of secondary oxygenate production relative to destruction.

Using detail from the MCM calculations indicate that surprisingly small subsets of hydrocarbon precursors are responsible for much of the in situ production of all three oxygenated species. Tables 3, 4 and 5 show the major precursor compounds for the in situ generation of acetone, methanol and acetaldehyde, respectively. Figures 8b, 9b and 10b show the speciated chemical formation rate of acetone, methanol and acetaldehyde, respectively, from point of emission day 1 to day 10 including some detail of the diurnal profile in the production rate of these compounds.

The individual reactions in the production process have been tracked using the MCM and Fig. 11 illustrates a typical flow chart showing acetaldehyde production routes 5 days after emission. All species show most rapid generation within the first 6–12 h following emission, however OVOC production rate as a function of time since emission does not follow the first order decay in precursor hydrocarbon concentration. Significant formation rates are maintained throughout the simulated 10-day chemical evolution sustained by the relatively long atmospheric lifetimes of some intermediate com-

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pounds formed in the degradation process. The formation of reservoir species such as organic peroxides and long chain alcohols coupled with the slow feed-through of higher molecular weight oxidation products, themselves generated from larger hydrocarbons extends the timescale for production very significantly beyond the lifetime of the original hydrocarbon precursor. It is significant that many of the longer lifetime intermediates such as organic peroxides and large alcohols are not currently measured, and their observations would be very beneficial in trying to determine the full extent of possible in situ production.

4. Conclusions

Observations of acetone, methanol, acetaldehyde and a range of non-methane hydrocarbons have been made in North Atlantic marine air at the Mace Head observatory. Acetone, methanol and acetaldehyde were found to be highly significant in terms of total mass of organics and their contribution to OH radical loss when compared with all other reactive organic compounds measured at this location. Deposition of methanol to the sea surface was suggested during a period of continued cyclonic activity (Carpenter et al., 2004), but there was no evidence within this dataset to suggest similar behaviour for acetone and acetaldehyde. Longer time series measurements would help to determine this conclusively. Chemical production routes for methanol, acetone and acetaldehyde were investigated and the key precursor species identified as a relatively small subset of non-methane hydrocarbons, in addition to other OVOCs. The large number of steps and the existence of stable oxidative intermediates in the in situ generation of OVOCs may explain both our observations and others, which have shown substantial concentrations of high reactivity OVOCs in airmasses that have been unperturbed for many days. A lack of observational techniques for these species is clearly a major gap in verifying such conclusions. The mechanisms for oxygenate production demonstrates that secondary chemistry must be explicitly considered when attempting to calculate the abundance of such species in the background atmosphere, and that the full accounting of high molecular weight species may well be essential if the feed-through of carbon to smaller forms such as these is to be correctly modelled.

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Table 1. Previous observations of acetaldehyde and acetone at selected rural sites together with this campaign

	acetaldehyde (ppbV)			acetone (ppbV)			Reference
	mean	max	min	mean	max	min	
Rural site, Georgia, US	0.70	3.80	–	1.80	6.70	–	Lee et al. (1995)
Marine site, Caribbean	0.50	0.94	0.21	0.40	0.63	0.18	Zhou and Mopper (1993)
South Germany	0.70	1.80	0.10	2.60	4.80	0.20	Slemr et al. (1996)
Mace Head	0.44	2.12	0.12	0.50	1.67	0.16	This study

Table 2. Initial concentrations of species used in the box model. Where: a corresponds to typical concentrations in the marine boundary layer and, b to values taken from the 3rd PORG report.

species	concentration (pptV)	Reference
carbon monoxide	110 000	a
nitric oxide	220	a
nitrogen dioxide	780	a
ozone	40 000	a
hydroxyl radical	0.066	a
hydroperoxy radical	4.94	a
methane	1 840 000	b
ethane	2300	b
butane	1605	b
acetylene	1064	b
ethene	958	b
2methyl butane	947	b
2-methyl propane	864	b
propane	824	b
methyl benzene	741	b
benzene	450	b
hexane	442	b
pentane	397	b
2-methyl pentane	392	b
3-methyl pentane	349	b
butene	269	b
2,2-dimethylpropane	241	b
1,2-dimethyl benzene	193	b
ethyl benzene	183	b
1,3-dimethyl benzene	179	b
1,4-dimethylbenzene	179	b
propene	143	b
isoprene	64	b
1-pentene	63	b
heptane	42	b
trans 2-butene	33	b
octane	30	b
cyclohexane	28	b
cis 2-butene	21	b
nonane	13	b
1,3-butadiene	12	b
1-hexene	9	b

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Table 3. Contribution of each parent hydrocarbon to the formation of acetone after 1, 5 and 10 days. Key intermediate species have been named where appropriate (see Appendix A for structures and nomenclature). Where X signifies the total of all other remaining sources.

		percentage acetone formation		
precursor	key intermediate	day1	day 5	day10
iso-pentane	direct	31.85	11.55	6.44
	IPECOOH	2.10	8.19	5.88
	MIPK	2.33	5.86	6.37
	MIPK and IC3H7OOH	1.03	2.20	1.03
iso-butane	direct	25.62	13.83	11.28
	TC4H9OOH	1.36	8.62	9.19
n-pentane	direct	1.36	1.02	2.03
	TC4H9OOH	0.07	0.64	1.90
propane	direct	13.19	6.32	7.39
	IC3H7OOH	5.85	16.12	20.25
2-methyl-pentane	direct	2.79	0.00	0.00
	M2PEDOOH	0.21	0.00	0.00
X		12.23	25.64	27.93

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Table 4. Contribution of each parent hydrocarbon to the formation of methanol after 1, 5 and 10 days. Key intermediate species have been named where appropriate (see Appendix A for structures and nomenclature). Where X signifies the total of all other remaining sources.

		percentage methanol formation		
precursor	key intermediate	day1	day 5	day10
methane	direct	50.00	64.00	75.00
iso-butane	direct	2.65	1.48	0.63
	TC4H9OOH	0.14	0.92	0.51
iso-pentane	direct	0.14	0.11	0.13
	TC4H9OOH	0.01	0.07	0.11
acetaldheyde	direct	14.28	12.50	6.30
X		32.78	20.92	17.33

Table 5. Contribution of each parent hydrocarbon to the formation of acetaldehyde after 1, 5 and 10 days. Key intermediate species have been named where appropriate (see Appendix A for structures and nomenclature). Where X signifies the total of all other remaining sources.

		percentage acetaldehyde formation		
precursor	key intermediate	day1	day 5	day10
n-butane	direct	13.41	18.92	21.08
iso-pentane	direct	11.29	11.28	6.23
ethane	direct	9.49	17.50	34.51
butene	direct	8.97	0.41	0.35
propene	direct	5.76	0.00	0.00
3-methyl-pentane	direct	5.11	4.62	1.87
propane	direct	3.82	4.440	6.32
pentene	direct	1.31	1.25	1.87
2-methyl-pentane	direct	1.17	0.68	0.00
X		39.67	41.48	27.78

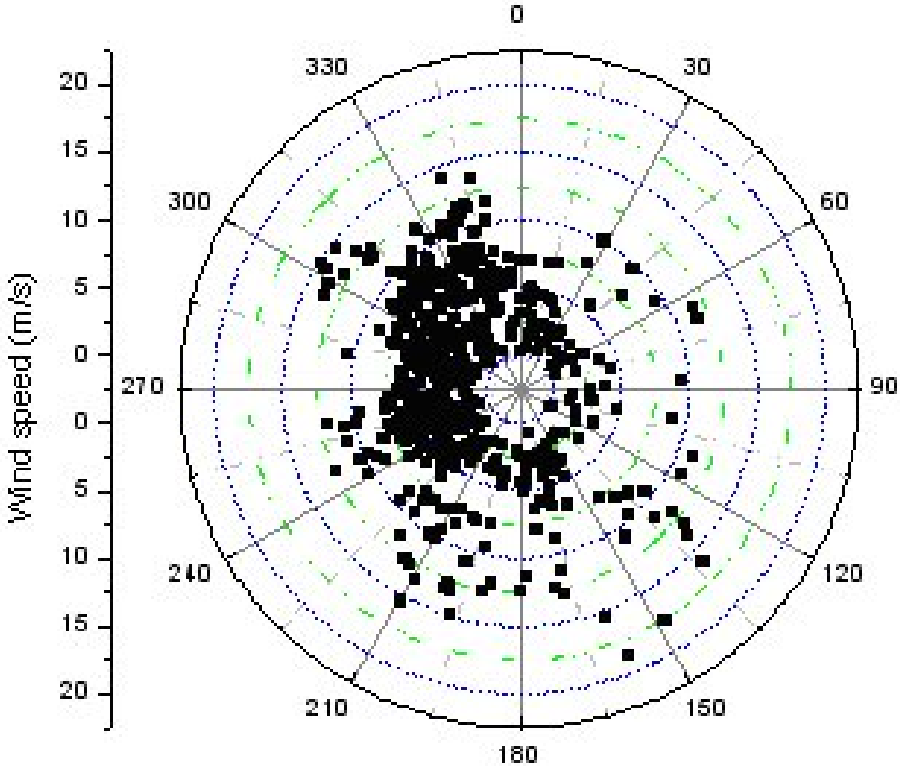

Fig. 1. Polar plot of local wind direction for organic observations during NAMBLEX 2002 experiment. Mace Head "clean" sector roughly 210° to 330° shows a significant number of samples allowing comprehensive study under these conditions.

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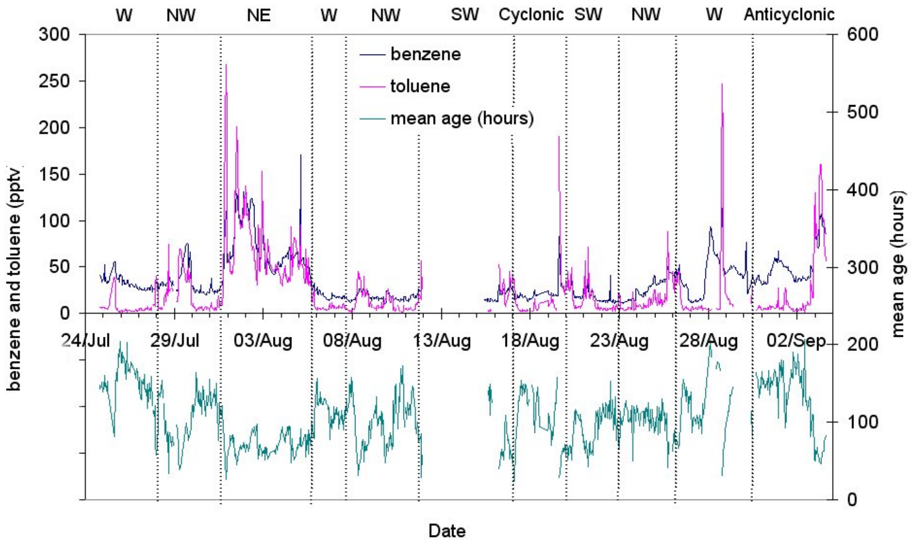

Fig. 2. Benzene and toluene observations versus Julian day 2002, used as markers for airmass pollution 'age' arriving at the site. (Assumes a starting ratio of 1:4.4 and $[OH]=1\times10^6$ molecules cm^{-3}, rate constants from Atkinson, 1986, 1989). Times series subdivided into periods with distinct airmass origins. Data with contradictory local wind direction/trajectory origin/chemical signatures were subsequently excluded from airmass type average calculations.

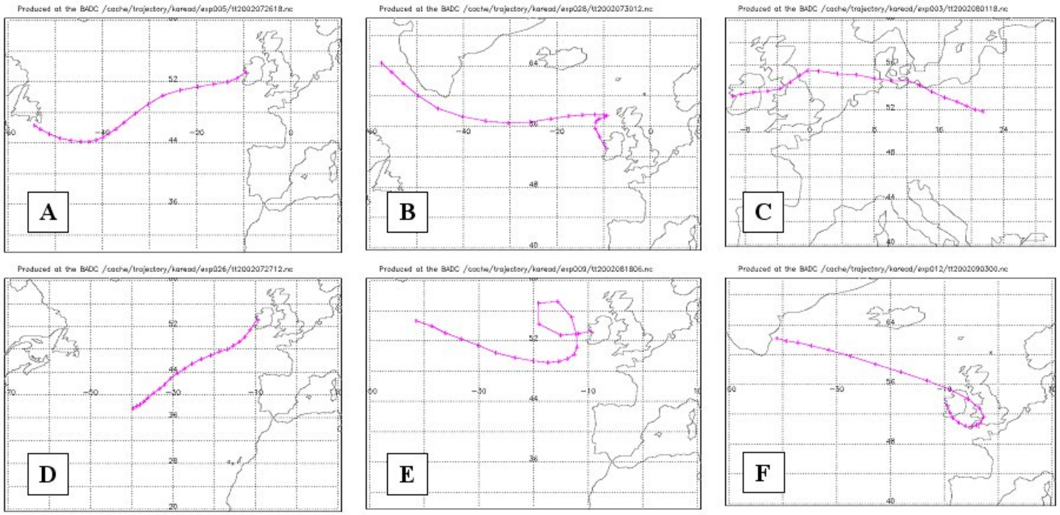

Fig. 3. Airmass trajectory classifications as used in Figs. 2 and 4, A=West (W), B=North West (NW), C=North East (NE), D=South West (SW), E=cyclonic, and F=anti cyclonic.

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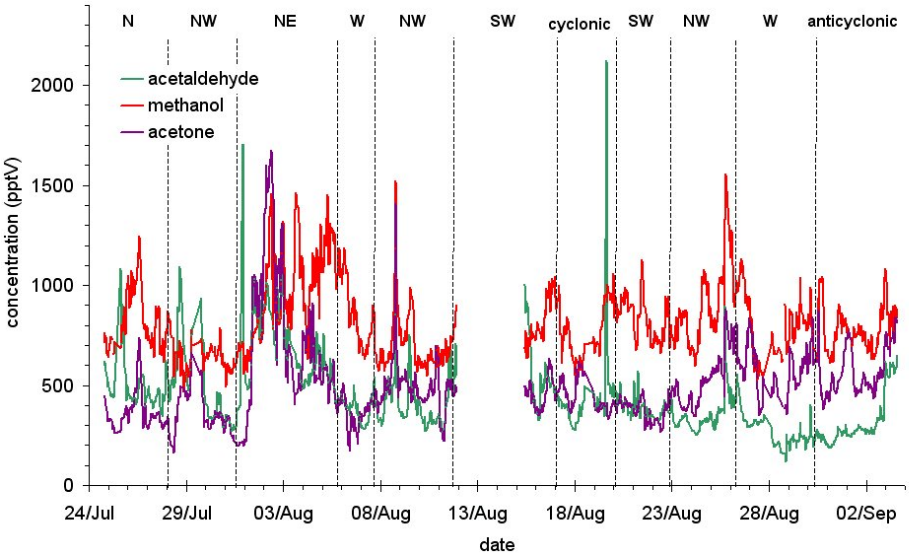

Fig. 4. Time series plot of acetaldehyde, methanol and acetone observed during the NAMBLEX campaign showing the high concentrations of these compounds under all conditions encountered.

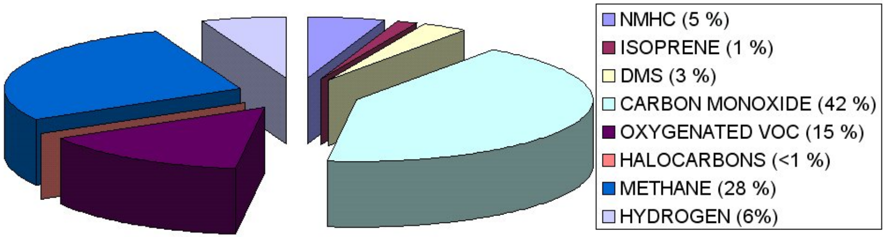

Fig. 5. Relative contribution to OH loss under clean southwesterly maritime conditions for NMHC, isoprene, dimethyl sulphide (DMS), carbon monoxide, oxygenated VOC (acetone+methanol+acetaldehyde), halocarbons and methane.

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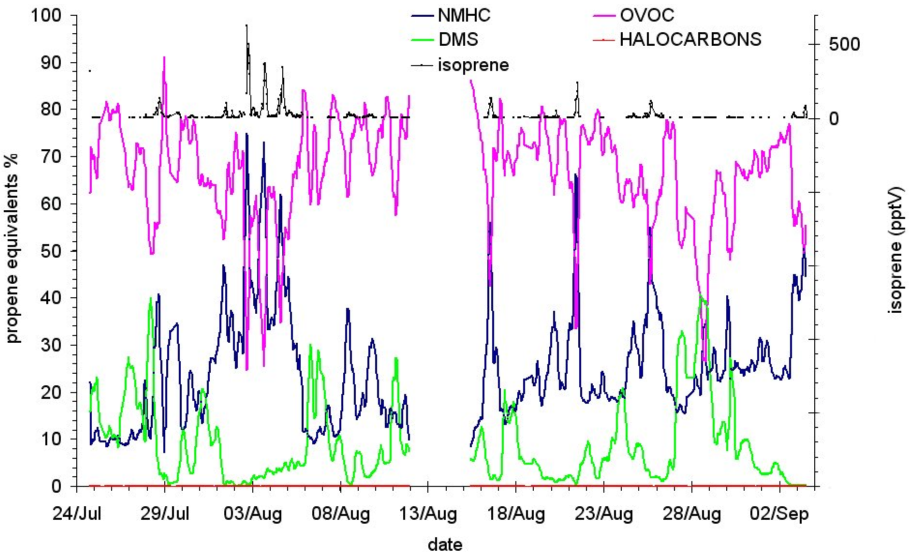

Fig. 6. Time series showing the percentage relative contribution as OH organic sinks for NMHC, DMS, OVOC and halocarbons ($CHCl_3$ + C_2Cl_4) calculated using OH-reactivity-scaled concentrations based on propylene equivalents. Oxygenated VOCs are clearly dominant, only when isoprene levels are high does the NMHC fraction become the largest sink. The halocarbons are of minor importance to OH loss under these conditions.

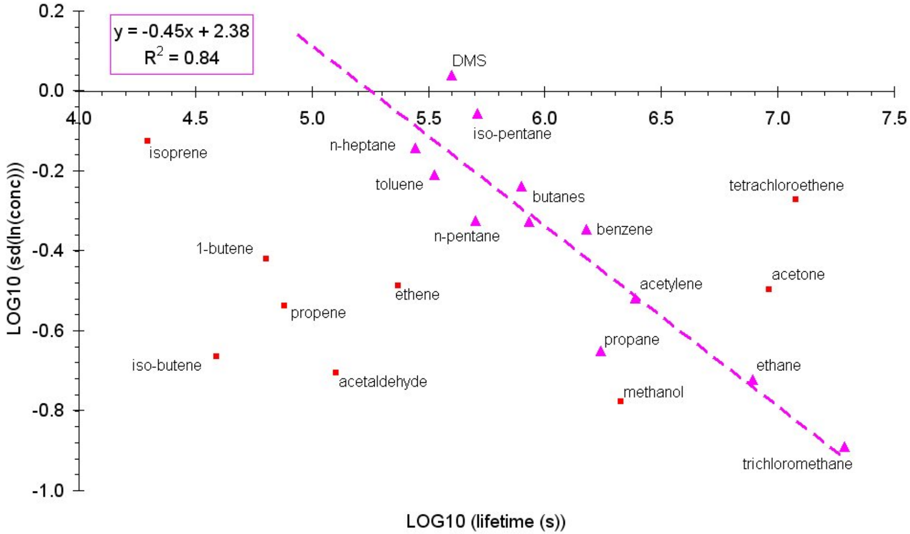

Fig. 7. Spatial variability-lifetime relationship for organic compounds in southwesterly air masses sampled during the NAMBLEX campaign. A linear relationship exists for some of the compounds implying common origin.

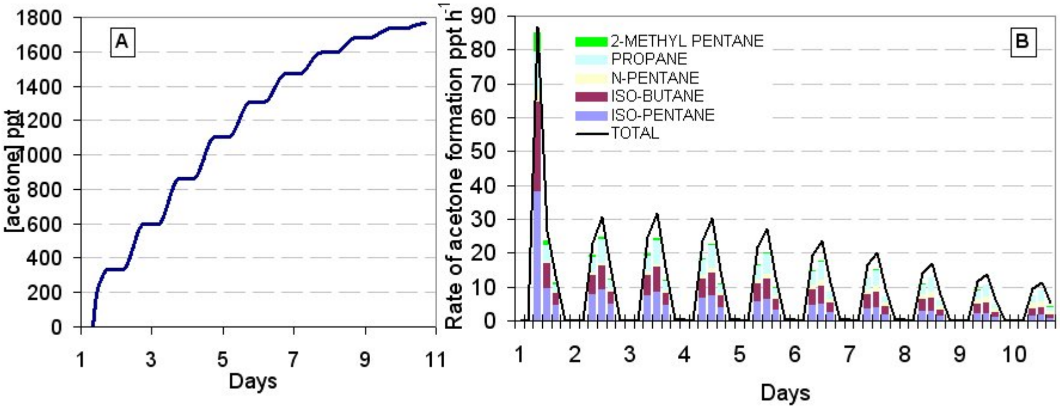

Fig. 8. **(A)** Box model calculation of acetone concentrations during 10 day airmass trajectory. **(B)** Total rate of acetone production in ppt h^{-1} (solid line) with individual precursor species contributions shown below as bar chart. Production exceeds destruction over the 10-day period.

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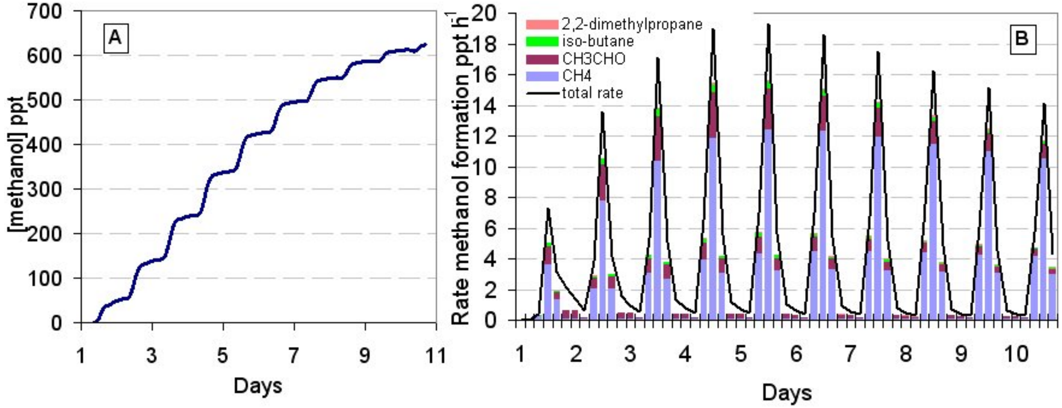

Fig. 9. (A) Box model calculation of methanol concentrations during 10 day airmass trajectory. **(B)** Total rate of methanol production in ppt h^{-1} (solid line) with individual precursor species contributions shown below as bar chart. Production exceeds destruction over the 10-day period.

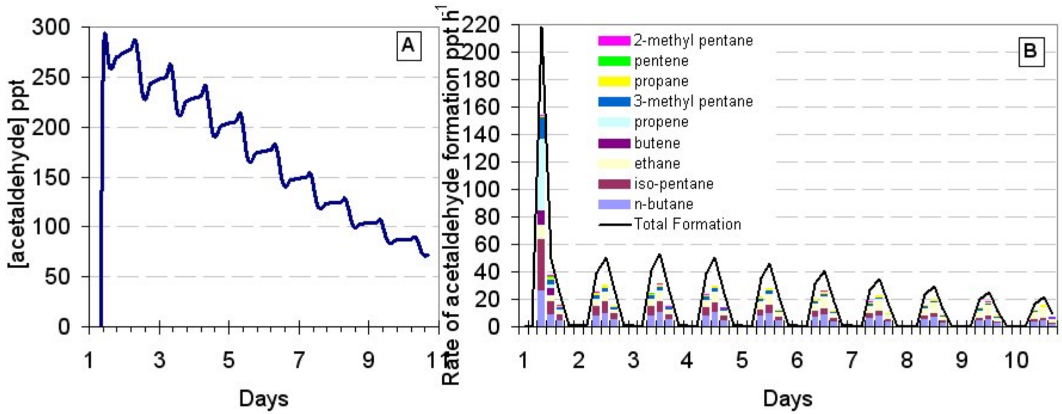

Fig. 10. **(A)** Box model calculation of acetaldehyde concentrations during 10 day airmass trajectory. **(B)** Total rate of acetaldehyde production in ppt h^{-1} (solid line) with individual precursor species contributions shown below as bar chart. Production initially exceeds destruction, however for the majority of the 10 day period there is a general reduction in atmospheric concentrations.

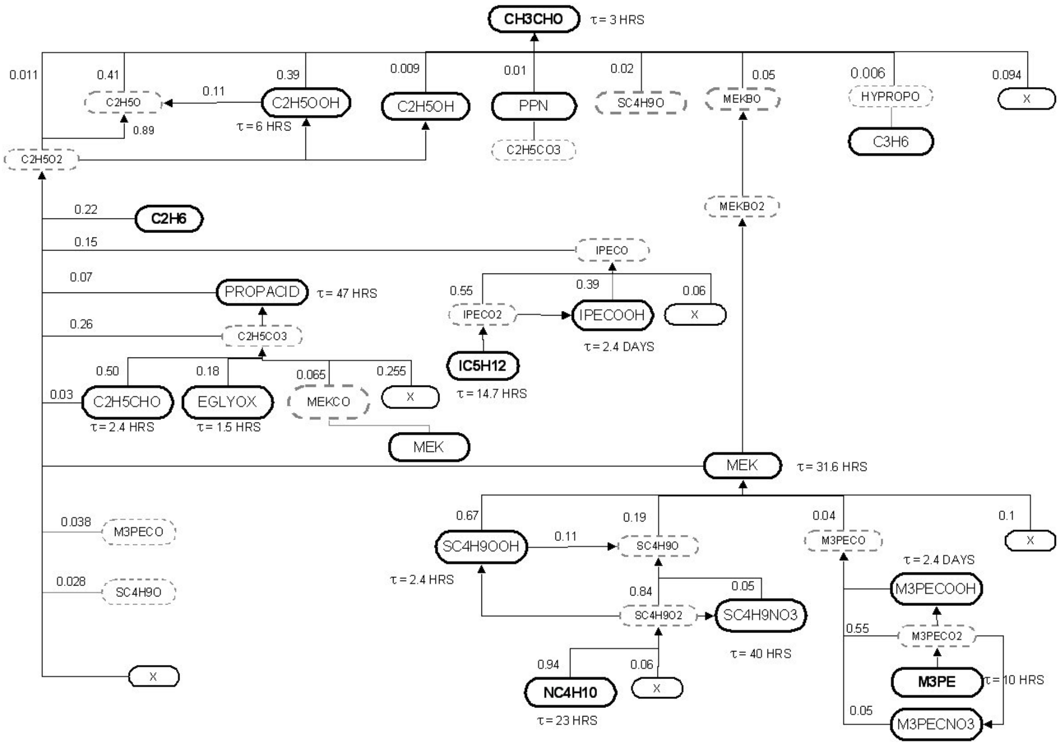

Fig. 11. Major sources of acetaldehyde on day 5. A solid border indicates stable species. The numbers on each branch signify the branching ratios for midday and the lifetimes given are also for midday. Structures and nomenclature of all species are given in Appendix A.

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Appendix A: Chemical structures and nomenclature

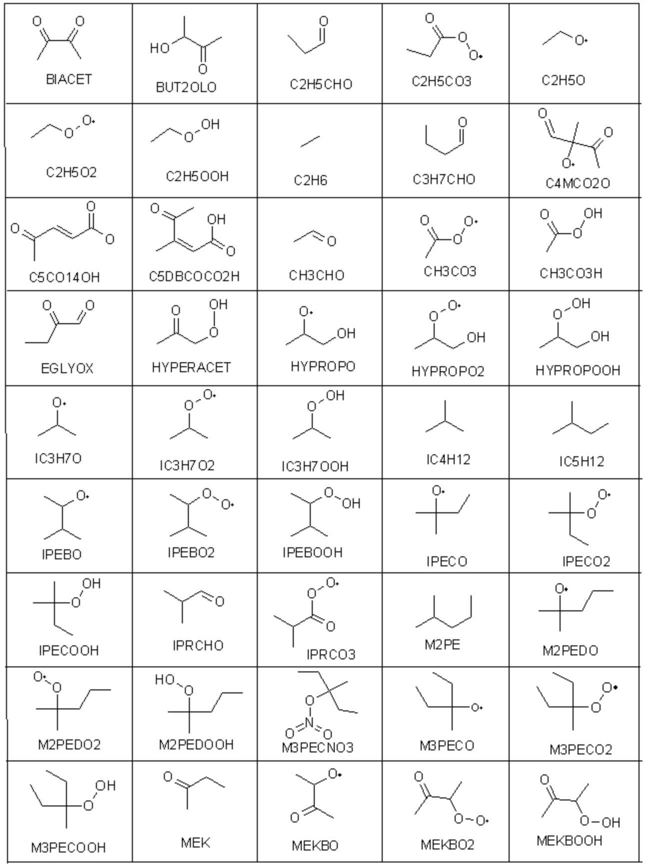

Fig. A1. Chemical structures and nomenclature for species used in the acetaldehyde production scheme shown in Fig. 11.

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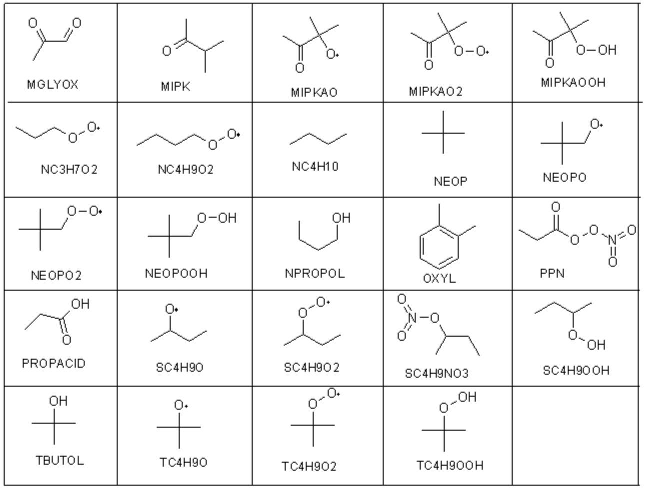

Fig. A2. Chemical structures and nomenclature for species used in the acetaldehyde production scheme shown in Fig. 11.

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